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Article *in* Environmental Pollution · January 2021

DOI: 10.1016/j.envpol.2020.115759

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Effects of hypolimnetic oxygenation on fish tissue mercury in reservoirs near the new Almaden Mining District, California, USA☆

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ARTICLE INFO

Article history:
Received 2 July 2020
Received in revised form
23 September 2020
Accepted 27 September 2020
Available online 12 October 2020

Keywords:
Methylmercury
Hypolimnetic oxygenation
Reservoir
Bioaccumulation

ABSTRACT

Almaden, Calero, and Guadalupe reservoirs (San Jose, CA, USA) are small (<13 million m^3) surface water reservoirs polluted by the former New Almaden Mining District, North America's most productive historical mercury (Hg) mine. Stevens Creek Reservoir (Cupertino, CA, USA) also has elevated fish Hg concentrations, but no historical mining source. We report a 15-year dataset to evaluate the effectiveness of line diffuser hypolimnetic oxygenation systems (HOSs) in reducing methylmercury (MeHg) concentrations in reservoir water and fish after four consecutive years of operation. HOSs were installed in each reservoir to increase dissolved oxygen concentrations in bottom water, thereby suppressing the activity of anaerobic bacteria (e.g., sulfate-reducing bacteria) known to produce MeHg. Before HOS operation, MeHg concentrations increased in bottom waters of all four reservoirs during periods of thermal stratification and profundal hypoxia. MeHg concentrations decreased significantly in bottom waters during HOS operation, with mean reductions of 63%–85% below pre-oxygenation concentrations. However, MeHg concentrations were unchanged or increased in surface waters. This could be the result of enhanced mixing between surface and bottom waters as a result of line diffuser oxygenation, or continued Hg methylation occurring in the oxic water column and littoral sediments. Despite little change in whole water column MeHg concentrations, we observed modest but significant declining trends in fish tissue Hg in Guadalupe and Stevens Creek reservoirs. Results suggest that oxygenation, rather than directly lowering MeHg in water, may have mixed nutrients into surface waters, thereby enhancing primary productivity and indirectly affecting Hg bioaccumulation by diluting concentrations in phytoplankton.

1. Introduction

Mercury (Hg) is a ubiquitous global environmental pollutant. Gaseous Hg is released to the atmosphere from anthropogenic (e.g. fossil fuel combustion) and natural (e.g. volcanoes) sources (Driscoll, 2013). Gold and Hg mine sites are often local Hg sources to the environment. Historical Hg mine sites (Almaden, Spain; Idrija, Slovenia; New Almaden, California) are contaminated with waste materials from Hg extraction processes (Nevado et al., 2003; Miklavčič et al., 2013; McKee et al., 2017). An estimated 4.5 million kg of Hg were lost to the environment from placer mines alone during the California Gold Rush of 1848–1855, contaminating watersheds of the western Sierra Nevada (Alpers et al., 2005). Mercury from atmospheric and mining sources can be transported into aquatic systems, where it can be microbially transformed into methylmercury (MeHg) and concentrated in aquatic food webs (Driscoll et al., 2013).

Methylmercury is a neurotoxin that presents health and reproductive risks to humans and wildlife that consume fish. In aquatic environments, Hg(II) complexes can be microbially converted to MeHg and released into the water column (Compeau and Bartha, 1985). Though sulfate-reducing bacteria are the predominant organisms implicated for MeHg production, any anaerobic organism containing the *hgcAB* gene cluster can facilitate the conversion of Hg(II) to MeHg (Gilmour et al., 2013). Methylmercury is produced at the sediment-water interface, accumulating in the anoxic bottom water of stratified lakes and reservoirs, and entering

☆ This paper has been recommended for acceptance by Wen-Xiong Wang.
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https://doi.org/10.1016/j.envpol.2020.115759

surface waters during fall destratification (Slotton et al., 1995; Herrin et al., 1998). Methylmercury can also be produced in the water column (Eckley and Hintelmann, 2006), often associated with settling particles in the metalimnion (Gascón Díez et al., 2016).

Methylmercury in the water column can adsorb to seston or enter phytoplankton cells, where it concentrates by up to five orders of magnitude relative to water concentrations (Pickhardt and Fisher, 2007). Following algal uptake, MeHg can concentrate up to an additional order of magnitude in each trophic step, reaching fish tissue concentrations that exceed water column concentrations by factors of millions (Lehnherr, 2014). Because relatively low concentrations of Hg in water and sediments can lead to harmful MeHg levels in fish, remediation strategies emphasize reducing the production and bioaccumulation of MeHg in addition to Hg source control (Eckley et al., 2020). Even minor reductions of MeHg concentrations in the water column or primary producers may significantly reduce concentrations in fish due to biomagnification effects (Pickhardt and Fisher, 2007).

Mercury accumulation in reservoir fish is a major human and ecological health concern in California, affecting about half of the reservoirs in the state (SWRCB, 2017a). Reservoir impairment severity varies with Hg source (Hg mining, gold mining, atmospheric deposition); reservoir physical, chemical, and biological characteristics; and reservoir operations (Hsu-Kim et al., 2018). High Hg in fish disproportionally affects Native American tribes and subsistence fishers who depend on locally caught fish for food security (SWRCB, 2017c). The State Water Resources Control Board is currently developing the Statewide Mercury Control Program for Reservoirs to address fish Hg levels that are unsafe for consumption by humans or wildlife (SWRCB, 2017b).

A thorough understanding of Hg dynamics in reservoirs is crucial to select effective remediation strategies. Various methods have been employed to decrease MeHg production in reservoirs by buffering redox potential at the sediment-water interface. Redox buffering aims to thermodynamically disfavor methylating organisms by providing excess terminal electron acceptors for bacteria that are not known methylators (aerobic, denitrifying, and manganese-reducing bacteria). Lake and reservoir pilot studies have used hypolimnetic addition of oxygen (Beutel et al., 2014; McCord et al., 2016) and liquid calcium nitrate (Matthews et al., 2013; Austin et al., 2016) to decrease sediment MeHg release. Manganese oxide amendments have been evaluated in experimental mesocosms, but not on a field scale (Vlassopoulos et al., 2018). Though these methods have shown promise in reducing MeHg concentrations in bottom waters, none have been found to conclusively reduce MeHg concentrations in fish independent of other remediation actions such as sediment dredging and capping. The objective of this study was to test the efficacy of line diffuser hypolimnetic oxygenation systems (HOSs) in reducing MeHg production and bioaccumulation in contaminated reservoirs. Oxic conditions at the sediment-water interface lowered MeHg concentrations in overlying water in experimental incubations using sediments collected from water bodies in the study watershed (Duvil et al., 2018). We apply this concept at the reservoir-scale, investigating the effects of oxygen addition on MeHg production and bioaccumulation in three reservoirs located near the historical New Almaden Hg mining district south of San Jose, California and a nearby reservoir uninfluenced by Hg mining.

2. Site and system description

2.1. Site description

The New Almaden Mining District (San Jose, CA, USA) was North America's largest and most productive Hg mine. The Guadalupe River watershed is contaminated with Hg waste from former mining operations. Despite about $10 million USD for remediation to excavate and contain processed ore, many waste piles and miles of polluted creeks have not yet been remediated. Consequently, typical annual Guadalupe River Hg transport from the mining district to San Francisco Bay is 120 kg/yr (McKee et al., 2017). Almaden (AR), Calero (CR), Guadalupe (GR), and Stevens Creek (SCR) reservoirs (Santa Clara County, CA, USA) are mesotrophic to eutrophic, monomictic reservoirs constructed in the mid-1930s (Fig. 1; Table S1). The reservoirs are used to capture local runoff for subsequent recharge of groundwater basins used for potable supply, and for flood protection. Almaden Reservoir and GR (Guadalupe River watershed) receive Hg mine waste from New Almaden, some of which is transported from AR to CR via Almaden-Calero Canal (Fig. 1) (Tetra Tech, 2005). Guadalupe Reservoir and AR receive water exclusively from their local watersheds. Calero Reservoir can receive water through a canal from AR or a pipeline from a large storage reservoir outside of the watershed fed with water from the San Joaquin/Sacramento Delta. Stevens Creek Reservoir is in the Stevens Creek Watershed, where there is no known Hg mine waste. Its water source is exclusively its local watershed, and it drains to San Francisco Bay. Mercury in SCR is assumed to come from a combination of geologic, local atmospheric (Rothenberg et al., 2010) and global atmospheric sources (SWRCB, 2017a). Mercury sources and fish Hg levels relative to sediment total Hg are provided in Supplemental Text S1 and S2. These different characteristics of Hg loading to the reservoirs are reflected in the relatively high sediment total Hg concentrations in AR and GR (Table 1).

Almaden Reservoir, GR, and SCR receive inflow from local precipitation during the wet season (November to April) and are drawn down over 50% by volume during the dry season. These reservoirs receive little to no summer inflow. In contrast, CR, which primarily receives imported water, is maintained at a more consistent capacity year-round. All four reservoirs have bottom-release outlets that discharge hypolimnetic water throughout the year.

Each reservoir exceeds regulatory thresholds for Hg concentrations in fish (SWRCB, 2017a). Mercury in largemouth bass, the top predator and a sport fish, ranges from 0.75 mg/kg in SCR to 4.9 mg/kg in GR (35 cm standardized size, muscle, wet weight, Tables 1 and S2); GR contains among the highest fish Hg concentrations in the USA.

2.2. Hypolimnetic oxygenation systems (HOS)

Line diffuser hypolimnetic oxygenation systems (HOSs) installed in AR, CR, GR, and SCR between 2011 and 2015 each deliver around 675 kg of high-purity (>90%) oxygen gas per day to each reservoir's hypolimnion (Fig. S1). Fine oxygen bubbles are discharged from diffuser lines extending between 305 and 610 m laterally on the reservoir bottoms. The systems are operated from the beginning of thermal stratification (April–May) until fall destratification (September–October). Systems were operated only intermittently from 2013 to 2015 due to technical challenges, but

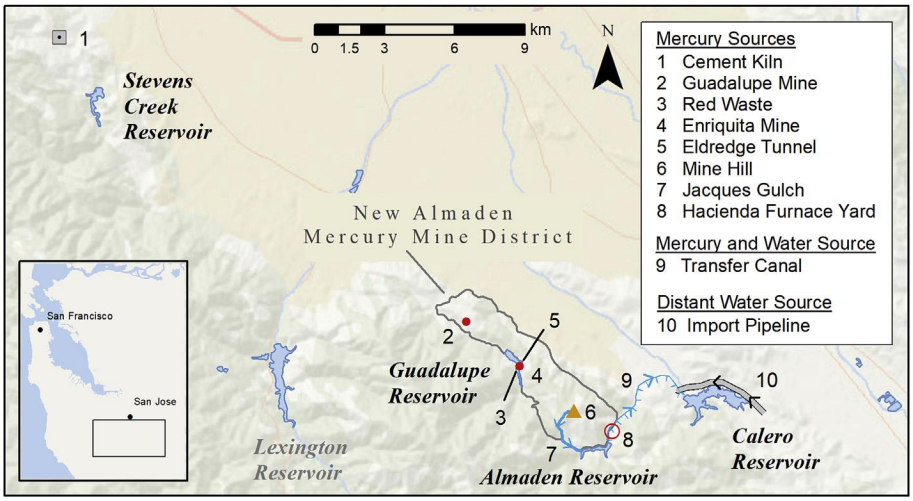

Fig. 1. Map of study site including Almaden, Calero, Guadalupe and Stevens Creek reservoirs, historical mercury mine locations, and hydrologic connectivity between reservoirs. Mercury sources are described in Supplemental Text S1.

Table 1
Select pre-HOS chemical characteristics of study site including Almaden, Calero, Guadalupe and Stevens Creek reservoirs. Values are mean and 95% confidence interval; sediment THg in dry weight and fish THg in wet weight. For sediment mercury samples, n = 2 for Stevens Creek Reservoir. Dry season (May-October) water samples, n = 48-84 for methylmercury and n = 39-71 for chlorophyll *a*.

Reservoir	MeHg (ng/L)[a]		THg (mg/kg, dry wt)		THg (mg/kg, wet wt)		Chlorophyll a (ug/L)
	Epilimnion	Hypolimnion	Sediments	n	35 cm bass*	Age-1 bass (whole)_	(2 m depth, dry season)
Almaden Reservoir	0.74 ± 0.1	1.86 ± 0.54	5.4[b]	1	2.8 ± 0.9	0.9 ± 0.09	3.39 ± 0.92
Calero Reservoir	0.24 ± 0.06	1.93 ± 0.52	0.42 ± 0.08[c]	18	1.1 ± 0.07	0.11 ± 0.02	8.5 ± 1.15
Guadalupe Reservoir	0.6 ± 0.12	12.05 ± 2.44	3.32 ± 0.9[c]	16	4.9 ± 1.8	0.75 ± 0.09	1.83 ± 0.2
Stevens Creek Reservoir	0.12 ± 0.03	0.76 ± 0.23	0.16 ± 0.01[d]	2	0.75 ± 0.13	0.1 ± 0.02	2.02 ± 0.48

*Muscle Tissue.
[a] Dry season (May-October) mean. See Table S3 for details.
[b] Data = 2001.
[c] Data: Tetra Tech, 2005.
[d] Data: 2018.

near-continuous summer operation was maintained throughout the 2016–2019 stratified periods.

3. Methods

3.1. Field methods

Vertical profiles for temperature, dissolved oxygen (DO), oxidation reduction potential (ORP, relative to Ag/AgCl reference electrodes), chlorophyll *a*, and phycocyanin were collected bi-weekly to monthly since 2005 using regularly calibrated Hydrolab® DS5 multiparameter sondes. We used a Wildco® horizontal VanDorn trace metal sampler to collect water samples from discrete depths with ultraclean handling methods (U.S. E.P.A., 1996). Water samples for total Hg and MeHg, sulfate, and ammonia were collected from surface (2 m depth) and profundal (1 m from sediments) waters, termed "surface" and "profundal/bottom" respectively. Additional MeHg samples were collected at the top, midpoint, and bottom of the thermocline.

Fish assemblage data and tissue samples were collected as water level permitted, from annually (2011–2013) to twice-annually (spring and summer 2016–2019). Fish were collected using a Smith Root Model-H electrofishing boat at four shoreline stations for 15-min passes. Black crappie (*Pomoxis nigromaculatus*), bluegill (*Lepomis macrochirus*), and largemouth bass (*Micropterus salmoides*) from 50 to 350 mm were euthanized using tricaine mesylate, and frozen for later analysis. Up to 42 fish samples were collected from each reservoir per sampling event, ideally collecting each species over the entire 50–350 mm length range. However, this was not always possible.

3.2. Analytical methods

Water samples were analyzed by Eurofins Scientific (Pleasanton, CA, USA). Total Hg was analyzed by EPA method 1631E (U.S. E.P.A., 2002). The method detection limit (calculated following 40 CFR 136, Appendix B) for total Hg is 0.2 ng/L. Total MeHg (unfiltered) was analyzed by EPA method 1630 (U.S. E.P.A., 1998). The method detection limit for MeHg is 0.02 ng/L. Strict quality control standards were followed for trace-level Hg and MeHg analysis, including method blanks, matrix spikes/matrix spike duplicates (method requirement = 75–125% recovery), and ongoing precision and recovery samples (method requirement = 77–123% recovery). Sulfate was analyzed by ion chromatography (U.S. E.P.A., 1993). Total Hg in fish tissue (whole body) and sediment were analyzed by Brooks Applied Labs (Seattle, Washington, USA) using a HNO_3/H_2SO_4 digestion, followed by EPA method 1631E (U.S. E.P.A., 2002). Frozen whole fish were defrosted and thoroughly homogenized using a clean blender prior to digestion. Fish Hg analysis followed strict quality control measures, including duplicates (acceptable relative percent difference = 30%), matrix spikes/matrix spike duplicates, and method blanks. Adequate recovery (75–125%) was

verified using certified reference material (TORT-3).

3.3. Statistical methods

Water quality data were evaluated by comparing dry season (May 1-September 30) measurements made prior to operation of HOS (OFF) to dry season measurements made during system operation (ON). Due to periodic shutdowns, the systems were considered ON if profundal dissolved oxygen concentrations were maintained above 2 mg/L. For data that were normally distributed, or could be normalized, Welch's *t*-test was used to compare between ON and OFF groups. The nonparametric Mann-Whitney test was used to compare ON and OFF groups that could not be normalized.

Due to limited fish Hg data prior to HOS operation, our evaluation consists of both before/after comparisons and trend analysis following HOS installation. We compared fish Hg data collected before and during HOS operation for each species in each reservoir. The post-HOS dataset for each species/reservoir combination consisted of the most recent samples collected in the same number and length range as the pre-HOS dataset. We length-standardized each individual fish to 100 mm by dividing its Hg concentration by its length, then multiplying by 100 mm. This approximation is valid because fish length is linearly associated with Hg concentration for each species on each sampling event (Fig. S2). Monson (2009) found this averaging method to be interchangeable with the commonly used least-squares method of length-standardization. We compared pre- and post-HOS length-standardized Hg concentrations in fish using the non-parametric Mann-Whitney test because data were not normally distributed and could not be transformed to fit a normal distribution.

Trends in fish Hg concentrations can be obscured by inconsistencies between field sample collections. Fish Hg varies with collection season, fish species, and fish length. While we made considerable effort to minimize variability during sampling events, this was not always possible. Several studies have used linear regression to assess trends in fish Hg over time (e.g. Monson, 2009; Monson et al., 2011; Gandhi et al., 2014). We used a multiple regression model to isolate the trend in fish Hg from the covarying factors based on the following (Eq. 1):

$$Hg = \beta_1 + \beta_2(Fish\ Species) + \beta_3(Fish\ Length) + \beta_4(Fish\ Species) \times (Fish\ Length) + \beta_5(Collection\ Season) + \beta_6(Sample\ Date)$$

The key parameter of interest is the Sample Date coefficient (β_6) because it represents the change in fish Hg with time. The model was applied to each reservoir using data collected following the onset of HOS operation.

To address uncertainty in the estimates of the Sample Date coefficients (β_6), we performed a nonparametric bootstrap analysis (r = 2000) to recalculate their 95% confidence intervals. Bootstrap analysis is a common method using resampling with replacement that can be applied to estimate confidence intervals of regression coefficients (Wu, 1986).

4. Results

4.1. Pre-oxygenation methylmercury production and fish tissue mercury

Each reservoir was thermally stratified annually from late spring (April–May) until early autumn (September–October). During stratification, profundal DO concentrations declined and MeHg concentrations increased. For example, in GR from June 2011 through September 2011, surface waters warmed to around 25 °C and anoxic profundal waters near the sediment-water interface contained over 20 ng/L MeHg, accounting for nearly 40% of the total Hg concentration (Fig. S3). Profundal MeHg buildup varied annually in each site, fluctuating with water quality conditions, water storage, and reservoir operations. In all reservoirs prior to oxygenation, MeHg buildup in bottom water corresponded with sulfate depletion and lower redox potential. In GR for example, bottom water in late summer exhibited sulfate minima typically <10 mg/L and MeHg maxima typically >20 ng/L when ORP was <100 mV (Fig. 2). Though AR and GR contained similar total Hg concentrations in sediment (~3–5 mg/kg, n = 1 and 16, respectively; see Supplemental Text S1 and S2 for different characteristics of Hg distribution in the reservoirs), average dry season MeHg concentrations prior to oxygenation in GR bottom water were an order of magnitude higher than AR (12.1 vs. 1.9 ng/L) (Table 1). AR and CR contained similar pre-oxygenation dry season mean MeHg concentrations in bottom water (1.9 ng/L), and SCR contained notably lower concentrations (0.8 ng/L). Pre-oxygenation dry season mean MeHg concentrations in surface water, an important source of MeHg to biota, were similar in AR and GR (0.6–0.8 ng/L), and lower in CR and SCR (<0.3 ng/L).

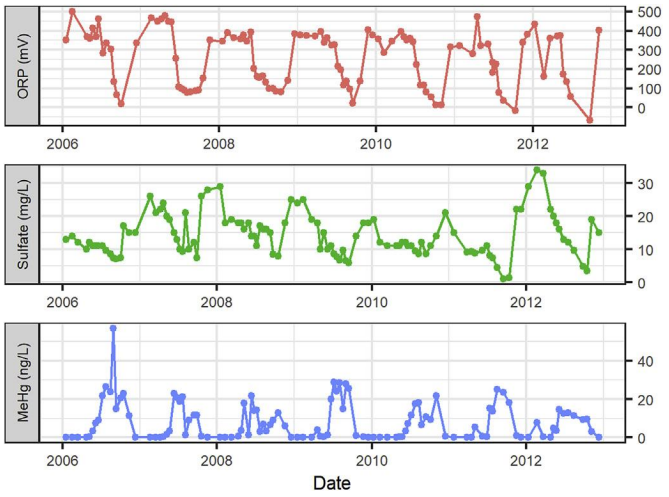

Fig. 2. Guadalupe Reservoir oxidation reduction potential (ORP) (top), sulfate (middle) and methylmercury (MeHg) from 2006- 2012 prior to oxygenation. Measurements were taken one meter from the reservoir bottom.

Though data collected prior to oxygenation were limited, mean Hg (whole body, wet weight) in age-1 largemouth bass was around 0.8 mg/kg in AR (n = 50) and GR (n = 11), and 0.1 mg/kg in CR (n = 52) and SCR (n = 7). Mercury (whole body, wet weight) in 35 cm length-standardized largemouth bass ranged from 0.75 mg/kg in SCR to 4.9 mg/kg in GR (Table 1). Additionally, fish Hg data were collected for bluegill, black crappie, and largemouth bass up to 350 mm (Table S2).

4.2. Oxygenation system operation

The hypolimnetic oxygenation systems were operated nearly continuously throughout the dry seasons of 2016–2019 (Fig. 3). DO saturation in bottom water increased significantly (Table S3, lines 41–48) in AR, GR, and SCR, from dry season means of 5–26% in years prior to oxygenation to means of 91–123% during oxygenation (Fig. S4). When reservoir oxygenation was initiated prior to the onset of profundal hypoxia (DO < 2 mg/L), anoxia was avoided, and oxygen-rich conditions were maintained throughout the stratification period. Though the diffuser lines extend only through the

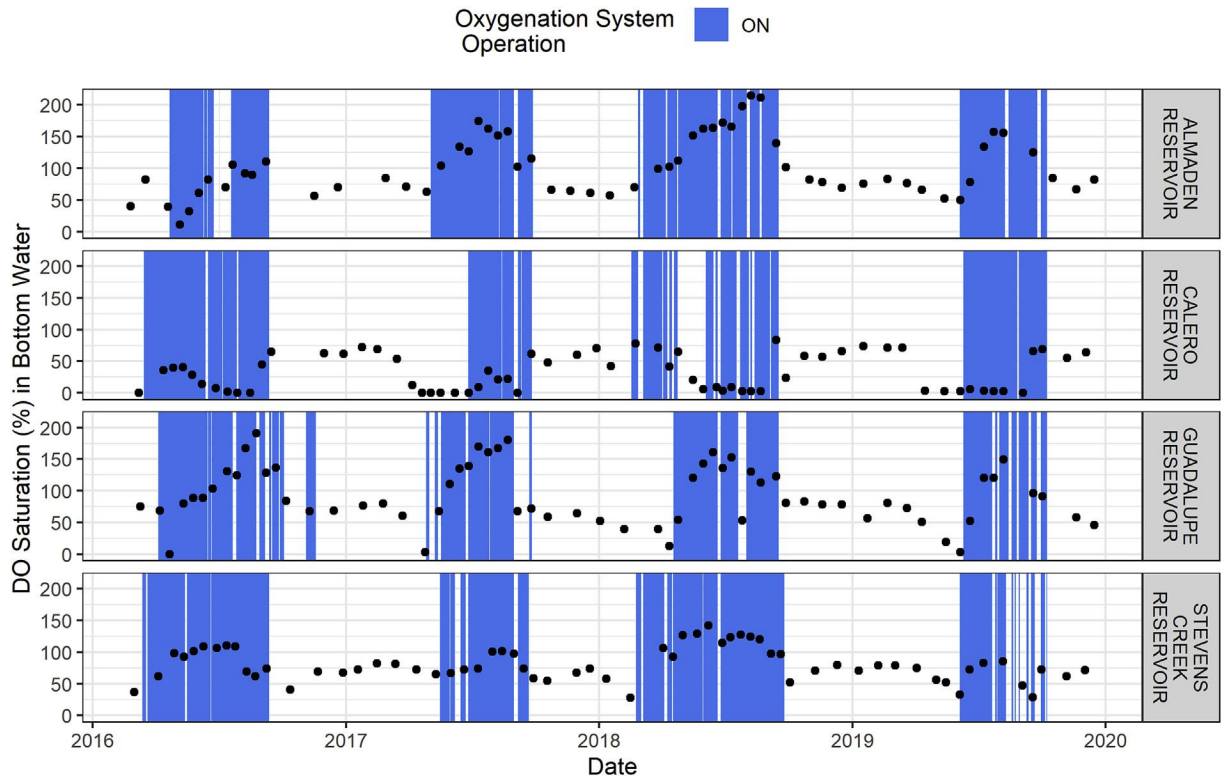

Fig. 3. Dissolved oxygen saturation in bottom water during oxygenation system operation.

deepest portions of the reservoirs, elevated DO concentrations propagated throughout the entire hypolimnion in all reservoirs except CR. For example, in June 2018, DO levels exceeded 14 mg/L throughout the hypolimnion of AR, including over 500 m away from the end of the oxygenation line diffuser (Fig. S5). DO saturation increased only modestly in CR, from a mean dry season saturation of 8.5% prior to oxygenation to 16.4% during oxygenation, with this effect limited to the immediate vicinity of the diffuser line (Fig. S4). Though this increase was statistically significant (Table S3, lines 43–44), the reservoir bottom experienced prolonged periods of anoxia during oxygenation (Fig. 3). As expected, surface water remained well-oxygenated throughout the year (mean dry season DO saturation; Table S3, lines 33–40, and Fig. S4).

4.3. Water quality results

In addition to DO, several water quality parameters of interest showed differences before and during oxygenation in bottom and surface water. Water temperatures increased significantly (Table S3, lines 105–112) in bottom water of all reservoirs except AR during oxygenation, with mean increases between 2.5 °C and 5.5 °C (Fig. S4). Surface temperature increased significantly (Table S3, lines 97–104) in CR, GR, and SCR, and nearly significantly in AR during oxygenation by about 1 °C (Fig. S4). During oxygenation, ORP unexpectedly decreased significantly in the bottom waters of AR and CR, and nearly significantly in GR (Table S3, lines 25–32) relative to previous years (Fig. S4). This effect was most pronounced in CR, where mean ORP decreased from 181 to 102 mV. In surface waters, mean ORP decreased significantly (Table S3, lines 17–24) by about 100 mV (Fig. S4). During oxygenation, mean sulfate concentrations were significantly higher in bottom waters of all reservoirs and in surface waters of all except AR (Table S3, lines 57–64; Fig. 4). Differences were modest, about 5 mg/L increase in CR surface and bottom waters (Fig. 4). Chlorophyll *a* concentration increased significantly (Table S3, lines 1–8) by 20–35% in the surface waters of all reservoirs except GR during oxygenation. This effect was most pronounced in CR, where the mean chlorophyll *a* concentration increased from 8.5 to 12.6 μg/L. Phycocyanin concentrations changed similarly, increasing by 25%–60% in the surface water of all reservoirs, with most notable increases in CR (Fig. S4).

Total Hg concentrations in bottom water were unchanged in GR but decreased significantly in AR, CR, and SCR (Table S3, lines 73–80) during oxygenation (Fig. 4). In SCR, total Hg concentrations in bottom water decreased from a dry season mean of 11.3 ng/L in years prior to oxygenation to 6.9 ng/L during oxygenation. Average total Hg concentrations decreased in surface waters of AR and GR (Table S3, lines 65–70). In GR, average total Hg concentrations decreased in surface waters from 13.8 to 6.6 ng/L (Table S3, lines 69–70 and Fig. 4).

Total MeHg decreased significantly (Table S3, lines 89–96) in the bottom waters of all reservoirs during oxygenation, with mean reductions from 63 to 85% below pre-oxygenation concentrations (Fig. 4). This effect was most pronounced in GR, where average concentrations decreased from 12.1 to 1.8 ng/L. However, MeHg concentrations were unchanged in surface waters, except for in SCR where concentrations increased slightly but significantly (Table S3, 81–88) from 0.12 to 0.15 ng/L (Fig. 4). Percent MeHg (MeHg/total Hg*100%), a coarse metric of methylation potential in aquatic ecosystems, decreased significantly in the bottom water of GR (mean values pre- and post-oxygenation: 34 vs. 9%) and SCR (15 vs. 6%), but was unchanged in AR and CR (Fig. S6). However, %MeHg values pre- and post-oxygenation increased by 3–5% in surface waters of all reservoirs except GR (Fig. S6). Methylmercury concentrations in the mid-water column were largely unchanged in all reservoirs. Whole lake MeHg concentration, calculated as the total

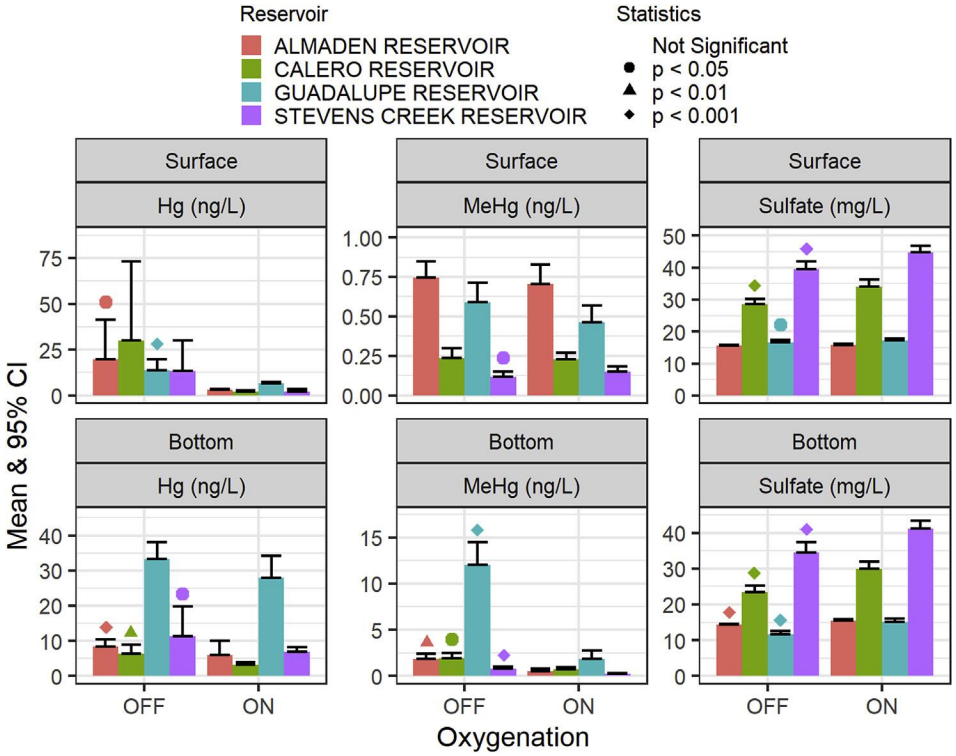

Fig. 4. Dry season methylmercury and related analytes measured prior to (OFF) and during (ON) oxygenation. "Surface" samples were taken two meters from the surface and "Bottom" samples were taken one meter from the bottom. Symbols above the OFF bar signify a significant difference between ON and OFF. See Table S3 for statistical results.

estimated mass of MeHg divided by the total water storage volume, increased significantly (Mann-Whitney test: U = 414, p-value = 0.005) in SCR from 0.10 ± 0.02 ng/L (n = 37; mean plus/minus 95% CI) prior to oxygenation to 0.17 ± 0.04 ng/L (n = 36) during oxygenation (Fig. S7). In GR, the whole lake MeHg concentrations decreased modestly, but significantly (Mann-Whitney test: U = 1704, p-value = 0.03) from 0.73 ± 0.16 ng/L (n = 61) to 0.70 ± 0.27 ng/L (n = 45) (Fig. S7). There were no significant changes in whole lake MeHg in AR or CR.

4.4. Fish tissue mercury

We found no significant difference between pre- and post-HOS 100 mm length-standardized fish Hg concentrations, except in AR where largemouth bass decreased by an average of 35%, and SCR where black crappie increased 114% (Table S4; Fig. 5). The Sample Date terms of the multiple regression model were significant ($p < 0.001$) and negative in GR and SCR (Table S5), indicating declining trends. To elucidate trends in fish Hg, we fit the regression models to 100 mm fish (Fig. 6, blue line). In GR and SCR, the bootstrapped 95% confidence intervals for the Sample Date coefficients (β_6) were comparable to the confidence intervals yielded by the multiple regression models (Table S6), confirming the declining trends. The 95% confidence intervals of the Sample Date coefficients (β_6) from both the regression and the bootstrap analysis did not overlap with zero, indicating that fish Hg in these reservoirs is declining with time. Since the beginning of HOS-operation, fish Hg has decreased in GR and SCR by 0.15 ± 0.02 mg/kg·yr and 0.02 ± 0.007 mg/kg·yr, respectively. This translates to decreases in Hg concentrations of 100 mm largemouth bass of about 55% in GR over seven years and 37% in SCR over five years of HOS operation.

5. Discussion

5.1. Oxygenation of profundal zone

Line-diffuser HOS was effective in oxygenating bottom waters in three of the four study reservoirs. DO concentrations were near or exceeded saturation throughout the profundal zone in AR, GR, and SCR. In contrast, the HOS in CR failed to overcome hypoxia (<2 mg/L). The delivery capacity of the CR HOS (675 kg O_2/day) was designed to exceed oxygen demands of 310 kg O_2/day, estimated using water column DO depletion rates from 1999 to 2002 (Brown and Caldwell, 2005). The original calculation appears to have underestimated true reservoir oxygen demands, which are highest in CR due to its large sediment surface area, longer water residence time, elevated trophic status, and weaker stratification.

Several factors may account for the relatively high oxygen demand in CR. CR is the most eutrophic reservoir studied, with notably higher nutrient and phytoplankton concentrations that increased during reservoir oxygenation (Fig. S4) (Seelos, 2017). Primary productivity increases sediment oxygen demand by supplying algal detritus rich in labile organic carbon and nutrients (N, P) to the profundal zone, where they stimulate microbial respiration (Beutel, 2003). It is plausible that the increased algal productivity observed in CR during HOS operation stimulated additional oxygen demand. Additionally, the mean increase in bottom water temperature of 2.4 °C during HOS operation is expected to increase sediment oxygen demand by around 20% (Zison et al., 1978). Increased turbulence and DO concentration at the sediment-water interface can enhance oxygen flux into sediment, a phenomenon known as induced oxygen demand (Beutel, 2003; Gantzer et al., 2009). This is especially the case in reservoirs like CR which has a relatively small hypolimnion thickness (i.e., high sediment area to volume ratio). In these reservoirs much of the settling organic

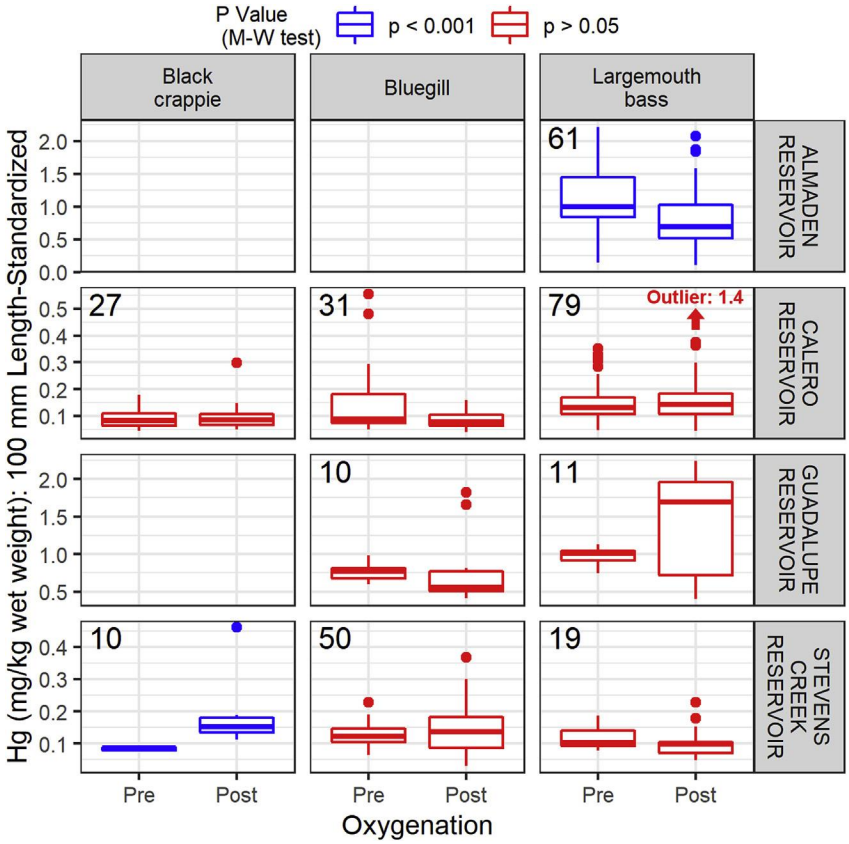

Fig. 5. Comparison of 100 mm length-standardized fish measured pre- and post-HOS operation. Fish were length-standardized using the "averaging" method described in Monson (2009). See Table S2 for statistical results. Numbers are sample size per group.

matter deposits on the sediment where it can induce oxygen demand (Beutel, 2003). Weakly-stratified reservoirs like Calero may also experience decreased retention of added oxygen by losing added oxygen to the upper water column (Moore et al., 2015).

While HOS was generally effective in enhancing DO in bottom waters, ORP exhibited counter-intuitive patterns. Line-diffuser HOS affected water chemistry in the profundal zone by oxidizing reduced compounds, altering microbial processes, and mixing some profundal waters throughout the water column. Surprisingly, profundal ORP either decreased or was unchanged during HOS operation. A shallow Georgia (USA) reservoir also exhibited lower ORP in surface and bottom waters during line diffuser HOS operation (Dr. David Austin, personal communication, 6/18/2020). This phenomenon may reflect enhanced mixing at the sediment-water interface, which could induce additional oxygen demand and release of reduced compounds from the sediments into the water column (Beutel, 2003). Delayed oxidation of Mn(II), and precipitation of Fe(II) and sulfide released from sediments could create the appearance of reduced conditions and potentially give relatively low ORP readings under oxygenated conditions. This agrees with other studies showing continued release of sulfide (oxidized to sulfate) (Duvil et al., 2018) and reduced metals from sediments under aerobic conditions (Gächter and Wehrli, 1998; Beutel et al., 2014). While our data suggest that some alteration of redox processes at the sediment-water interface did occur, these effects appear to be obscured by mixing and dilution of redox-sensitive compounds in the hypolimnetic water column caused by HOS-induced turbulence.

5.2. Water quality impacts during HOS operation

Water quality in reservoirs generally declined after HOS operation, results that differ from other studies (Beutel and Horne, 1999; Horne et al., 2019). Line-diffuser HOS appears to have introduced profundal compounds into the upper water column through enhanced mixing at the thermocline due to turbulence associated with a rising bubble plume along the length of the diffuser line (Gantzer et al., 2009). Despite unchanged profundal total phosphorus in all reservoirs except GR during oxygenation, total phosphorus concentrations increased significantly in surface waters of all reservoirs (Seelos, 2017). Because these reservoirs experience little to no external loading during HOS operation, these increases are likely internal in origin. We suggest that profundal nutrients, likely including phosphate, ammonia, and Fe(II), a key cyanobacteria micro nutrient, were transported into the photic zone with rising bubble plumes. Bottom water temperature increased between 2.5 °C and 5.5 °C on average during line-diffuser HOS operation. Notable increases in chlorophyll *a* and phycocyanin during HOS operation suggest that temperature and nutrient increases stimulated algal productivity (Correll, 1999; Singh and Singh, 2015; Konopka and Brock, 1978). Elevated DO saturation in surface water during HOS operation is additional evidence of water transfer between the profundal zone and surface waters, but also may be the result of higher algal productivity.

Reservoir outlet turbidity increased in SCR during HOS operation (Fig. S8). This was probably due to sediment entrainment from turbulent mixing (Moore et al., 2015). This effect was probably limited to SCR due to its erosive geology, consisting mainly of silt- and sandstones. Increased outlet temperature and turbidity present

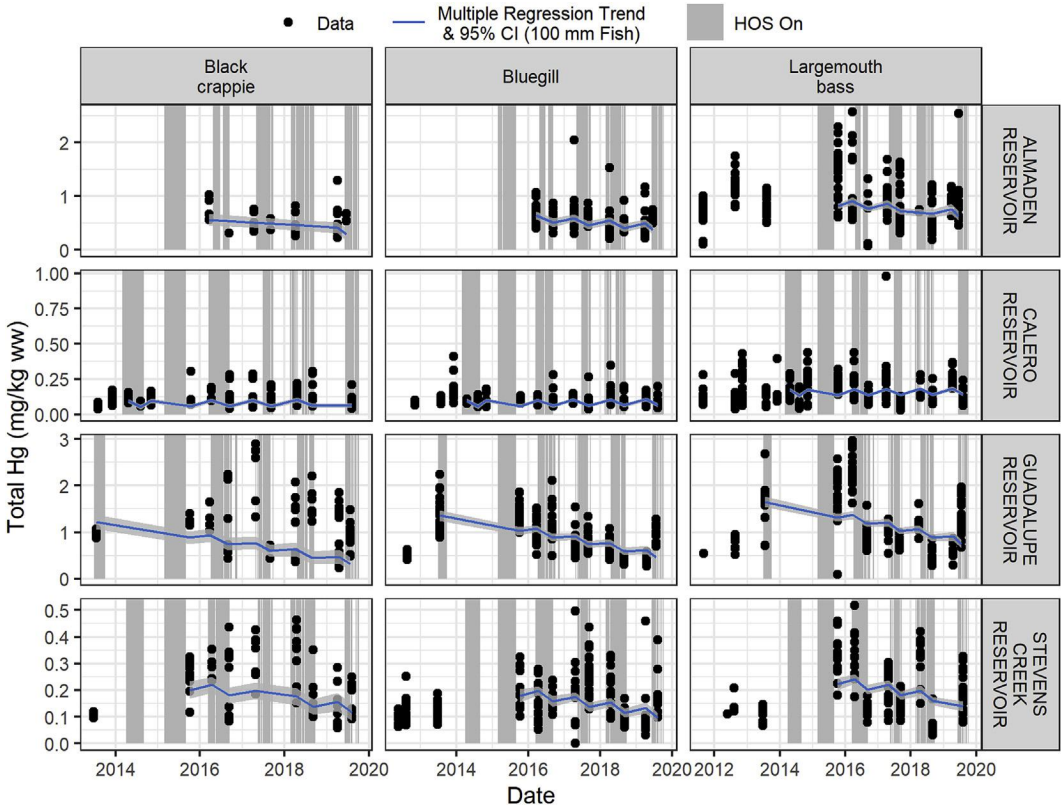

Fig. 6. Raw Fish Hg data (black dots) and multiple regression model fitted to 100 mm fish length. Guadalupe and Stevens Creek reservoirs have significant declining trends in fish Hg since the beginning of HOS operation. (Gaps in monitoring, e.g., 2013-2015, were due to drought.)

concerns when reservoirs discharge to waterways hosting salmonids, which are sensitive to these factors (Lehman et al., 2017). Though water quality may be improved during oxygenation, increases in outlet temperature and suspended sediment concentration could have negative effects in reservoir tail waters.

5.3. Water column methylmercury

Despite significant MeHg reductions in bottom waters, which averaged 63–85% across the study sites, average MeHg concentrations in the surface waters were unchanged in all reservoirs except SCR, where concentrations increased during HOS operation by 25%. Methylmercury in surface waters is of concern, because bioaccumulation occurs largely in the photic zone (Wu et al., 2019), and can be more pronounced in pelagic food webs (Stewart et al., 2008; Chen et al., 2014). Average water column MeHg concentrations, estimated as the mass of MeHg in water column divided by total water storage volume, were relatively unchanged during HOS operation, except in SCR, where they increased. Because there is no inflow during HOS operation, observations suggest that HOS did not substantially reduce net MeHg production and buildup in reservoir waters. These results call into question the mechanism by which MeHg concentrations were lessened in bottom waters. It appears that the observed reductions in profundal MeHg concentrations were mainly due to dilution and mixing effects, as opposed to redox-related inhibition of methylating bacteria. In addition, MeHg production in the oxic water column and littoral sediments were likely not inhibited by HOS operation and may account for the unchanged surface water MeHg concentrations. In fact, observed increases in the %MeHg in surface waters pre- and post-HOS in three of four reservoirs suggest that HOS operation may have enhanced MeHg production in surface waters. Several studies have shown MeHg production in the oxic water column, often associated with settling particles (Eckley and Hintelmann, 2006; Achá and Hintelmann, 2012; Gascón Díez et al., 2016), and in littoral sediments (Krabbenhoft et al., 1998).

Methylmercury accumulates in profundal waters during periods of thermal stratification, then enters pelagic biota during fall turnover (Slotton et al., 1995; Herrin et al., 1998). Slotton et al. (1995) measured 70–200% increases in juvenile largemouth bass Hg with the seasonal entrainment of upper hypolimnion water prior to turnover in Davis Creek Reservoir, a California reservoir polluted by Hg mining that discharges from the surface. Thus, management strategies that can decrease MeHg buildup in summertime bottom waters should yield lower levels of fall bioaccumulation. However, other studies have failed to observe increased MeHg concentrations in surface waters when lakes destratify (Regnell et al., 1997; Valdes et al., 2017). In our study reservoirs prior to HOS operation, fall reservoir destratification is unlikely to control the introduction of MeHg into our study reservoir food webs. Profundal MeHg concentrations typically peaked in August at redox potentials from 0 to 100 mV, then declined until destratification as highly reducing conditions established (e.g. GR, Fig. 2). This agrees with other studies noting a “Goldilocks” zone for MeHg production, after which sulfide inhibition and demethylation prevail (Benoit et al., 1999; Beutel et al., 2020; Oremland et al., 1991). By the time the reservoirs mixed between September and October, profundal MeHg decreased notably relative to the seasonal maximum concentrations, limiting MeHg available to the upper water column (Fig. 2). The study reservoirs contain bottom-release outlets that discharged MeHg-rich profundal water constantly and acted to dampen MeHg buildup in bottom waters. Mass balance

calculations, in which we compared over 200 discrete sampling dates collected before HOS operation during the stratified season, show that fall mixing would minimally (1–3%) increase photic zone MeHg concentrations, confirming that destratification is unlikely to control bioaccumulation in these reservoirs. HOS would be more effective in reservoirs that release water from the surface or mid-water column.

5.4. Mercury reductions in fish tissue

Though only largemouth bass in AR contain Hg concentrations that are lower than pre-HOS data, fish Hg in GR and SCR has been declining during HOS operation despite an initial increase compared to pre-HOS (Fig. 6). Initial increases in fish Hg were likely due to changes in MeHg production and bioaccumulation during the peak of the California Drought of 2011–2017. Fish Hg could have increased in this period as a result of greater MeHg production due to sulfate regeneration (Coleman Wasik, 2015; Eckley et al., 2017), temperature increases (Callister and Winfrey, 1986), or increased autochthonous carbon loading from algae blooms (Bravo et al., 2017). High water temperatures may also increase Hg bioaccumulation by altering fish metabolism, growth rate, and feeding patterns (Dijkstra et al., 2013).

Although this is the first study to show declining trends in fish Hg concentrations in oxygenated reservoirs, the mechanisms by which this occurred in GR and SCR remain unclear. The fact that significant decreases in fish Hg in GR and SCR corresponded with significant decreases in %MeHg pre- and post-HOS suggests that oxygenation lowered the potential for MeHg production in the profundal zone, which may have translated into lower bioaccumulation. However, because surface MeHg concentrations were not significantly different during HOS operation and Hg concentrations in fish have declined in these reservoirs, bioconcentration factors have decreased. Primary productivity increased in all reservoirs during HOS operation. Higher phytoplankton and biomass could result in Hg reductions by somatic growth dilution in zooplankton (Karimi et al., 2007) and fish (Ward et al., 2010). Additionally, increased phytoplankton and cyanobacteria given constant MeHg concentration may support “bloom dilution” that reduces MeHg uptake into pelagic food webs (Pickhardt et al., 2002). Significant increases in surface water chlorophyll *a* and phycocyanin during oxygenation may have caused reductions in fish Hg by diluting MeHg concentrations in phytoplankton, and encouraging rapid, efficient growth in zooplankton and fish. Furthermore, aerobic hypolimnia likely increased benthic habitat area, potentially providing benthic prey with lower MeHg concentrations than pelagic sources (Stewart et al., 2008). The similar, short aquatic food webs of GR and SCR support fewer trophic linkages, which may reduce biomagnification (Cabana and Tremblay, 1994). Shorter food webs may also respond faster to changes in water chemistry, which could be the reason we have not observed lower fish Hg in AR. In contrast, fish Hg in CR was likely unchanged due to the poor performance of its HOS.

6. Conclusion

We studied effects of line-diffuser HOS on MeHg production and bioaccumulation in three mercury mine polluted reservoirs (Almaden, Calero, and Guadalupe Reservoirs) and in another (Stevens Creek Reservoir). HOS was effective at oxygenating bottom waters in Almaden, Guadalupe, and Stevens Creek reservoirs. The HOS at Calero Reservoir did not increase DO concentrations above hypoxic levels (<2 mg/L) due to the reservoir’s greater oxygen demand and lower retention of added oxygen. Though MeHg concentrations decreased significantly in bottom waters, 63%–85% on average, concentrations in the photic zone were unchanged (Almaden, Calero, and Guadalupe reservoirs) or increased (Stevens Creek Reservoir). This may be due to enhanced exchange of profundal MeHg into the photic zone due to turbulent mixing caused by HOS operation, and/or continued MeHg production in the water column and littoral sediments. Fish Hg did not decrease in before/after comparison of most species, but in Stevens Creek Reservoir surface water MeHg and Hg in one of three fish species sampled increased, likely due to oxygenation. During four years of HOS operation, we observed statistically significant declining trends in fish Hg in Guadalupe and Stevens Creek reservoirs. We suspect that higher phytoplankton concentrations observed during HOS operation may have led to biodilution of MeHg, contributing to the observed decreases in fish Hg.

With regards to HOS implementation in small reservoirs, our experience suggests that care must be taken to properly size systems for potentially unanticipated oxygen demands. Line-diffuser HOS can enhance transport of compounds from bottom to surface waters, which may have unanticipated ecosystem consequences. Line-diffuser systems may need to consist of longer lines run at low discharge rates to minimize this effect. Alternatively, systems that minimize vertical turbulence while oxygenating, such as side-stream oxygen contact chambers, either on the shore or at the reservoir bottom, should be considered. Finally, future studies should focus on assessing profundal versus pelagic/littoral sources of MeHg to inform development and implementation of strategies to reduce Hg bioaccumulation in lakes and reservoirs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was funded by Valley Water’s Safe, Clean Water and Natural Flood Protection Program. Valley Water thanks our partners (Santa Clara County Parks, Midpeninsula Regional Open Space District, Waste Management) for continued collaboration in addressing legacy mercury pollution in the south San Francisco Bay. The views expressed herein are solely those of the authors and do not represent official policies or positions of their agencies.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.115759.

References

Achá, D., Hintelmann, H., Pabón, C.A., 2012. Sulfate-reducing bacteria and mercury methylation in the water column of the lake 658 of the experimental lake area. Geomicrobiol. J. 29 (7), 667–674. https://doi.org/10.1080/01490451.2011.606289.

Alpers, C.N., Hunerlach, M.P., May, J.T., 2005. Mercury Contamination from Historical Gold Mining in California. Environmental Health (October).

Austin, D., Scharf, R., Carroll, J., Enochs, M., 2016. Suppression of hypolimnetic methylmercury accumulation by liquid calcium nitrate amendment: redox dynamics and fate of nitrate. Lake Reservoir Manag. 32 (1), 61–73.

Benoit, J.M., Mason, R.P., Gilmour, C.C., 1999. Estimation of mercury-sulfide speciation in sediment pore waters using octanol-water partitioning and implications for availability to methylating bacteria. Environ. Toxicol. Chem. 18 (10), 2138–2141. https://doi.org/10.1897/1551-5028(1999)018<2138:EOMSSI>2.3.CO;2.

Beutel, M.W., 2003. Hypolimnetic anoxia and sediment oxygen demand in California drinking water reservoirs. Lake Reservoir Manag. 19 (3), 208–221. https://doi.org/10.1080/07438140309354086.

Beutel, M.W., Horne, A.J., 1999. A review of the effects of hypolimnetic oxygenation on lake and reservoir water quality. Lake Reservoir Manag. 15 (4), 285–297. https://doi.org/10.1080/07438149909354124.

Beutel, M.W., Dent, S., Reed, B., Marshall, P., Gebremariam, S., Moore, B., et al., 2014. Effects of hypolimnetic oxygen addition on mercury bioaccumulation in Twin Lakes, Washington, USA. Sci. Total Environ. 496, 688–700. https://doi.org/10.1016/j.scitotenv.2014.06.117.

Beutel, M.W., Fuhrmann, B., Herbon, G., Chow, A., Brower, S., Pasek, J., 2020. Cycling of Methylmercury and Other Redox-Sensitive Compounds in the Profundal Zone of a Hypereutrophic Water Supply Reservoir. Hydrobiologia, (in press).

Bravo, A., Bouchet, S., Tolu, J., et al., 2017. Molecular composition of organic matter controls methylmercury formation in boreal lakes. Nat. Commun. 8, 14255. https://doi.org/10.1038/ncomms14255.

Brown, Caldwell, 2005. Reservoir Aeration/oxygenation Study Agreement.

Callister, S.M., Winfrey, M.R., 1986. Microbial methylation of mercury in upper Wisconsin river sediments. Water Air Soil Pollut. 29, 453–465. https://doi.org/10.1007/BF00283450.

Cabana, G., Tremblay, A., Kalff, J., Rasmussen, J.B., 1994. Pelagic food chain structure in Ontario lakes: a determinant of mercury levels in lake trout (Salvelinus namaycush). Can. J. Fish. Aquat. Sci. https://doi.org/10.1139/f94-039.

Chen, Celia Y., et al., 2014. Benthic and pelagic pathways of methylmercury bioaccumulation in estuarine food webs of the northeast United States. PloS One 9, 2. https://doi.org/10.1371/journal.pone.0089305 e89305. 18 Feb.

Coleman Wasik, J.K., Engstrom, D.R., Mitchell, C.P.J., Swain, E.B., Monson, B.A., Balogh, S.J., Jeremiason, J.D., Branfireun, B.A., Kolka, R.K., Almendinger, J.E., 2015. The effects of hydrologic fluctuation and sulfate regeneration on mercury cycling in an experimental peatland. J. Geophys. Res. Biogeosci. 120, 1697–1715. https://doi.org/10.1002/2015JG002993.

Compeau, G.C., Bartha, R., 1985. Sulfate-reducing bacteria: principal methylators of mercury in anoxic estuarine sediment. Appl. Environ. Microbiol. 50 (2), 498–502.

Correll, D.L., 1999. Phosphorus: a rate limiting nutrient in surface waters. Poultry Sci. 78 (5), 674–682. https://doi.org/10.1093/ps/78.5.674.

Dijkstra, J.A., Buckman, K.L., Ward, D., Evans, D.W., Dionne, M., et al., 2013. Experimental and natural warming elevates mercury concentrations in estuarine fish. PloS One 8 (3), e58401. https://doi.org/10.1371/journal.pone.0058401.

Driscoll, C.T., Mason, R.P., Chan, H.M., Jacob, D.J., Pirrone, N., 2013. Mercury as a global pollutant: sources, pathways, and effects. Environ. Sci. Technol. 47 (10), 4967–4983. https://doi.org/10.1021/es305071v.

Duvil, R., Beutel, M., Fuhrmann, B., Seelos, M., 2018. Effect of oxygen, nitrate and aluminum addition on methylmercury efflux from mine-impacted reservoir sediment. Water Res. 144 (1), 740–751. https://doi.org/10.1016/j.watres.2018.07.071.

Eckley, C.S., Hintelmann, H., 2006. Determination of mercury methylation potentials in the water column of lakes across Canada. Sci. Total Environ. 368 (1), 111–125. https://doi.org/10.1016/j.scitotenv.2005.09.042.

Eckley, C.S., Luxton, T.P., Goetz, J., McKernan, J., 2017. Water-level fluctuations influence sediment porewater chemistry and methylmercury production in a flood-control reservoir. Environ. Pollut. (Barking, Essex: 1987) 222, 32–41. https://doi.org/10.1016/j.envpol.2017.01.010.

Eckley, C.S., Gilmour, C.C., Janssen, S., Luxton, T.P., Randall, P.M., Whalin, L., Austin, C., 2020. The assessment and remediation of mercury contaminated sites: a review of current approaches. Sci. Total Environ. 707, 136031. https://doi.org/10.1016/j.scitotenv.2019.136031. ISSN 0048-9697.

Gächter, R., Wehrli, B., 1998. Ten years of artificial mixing and oxygenation: No effect on the internal phosphorus loading of two eutrophic lakes. Environ. Sci. Technol. 32 (23), 3659–3665. https://doi.org/10.1021/es980418l.

Gandhi, N., Tang, R., Bhavsar, S., Arhonditsis, G., 2014. Fish mercury levels appear to Be increasing lately: a report from 40 Years of monitoring in the province of Ontario. Canada Environ. Sci. Technol. 48 (10), 5404–5414. https://doi.org/10.1021/es403651x, 2014.

Gantzer, P.A., Bryant, L.D., Little, J.C., 2009. Effect of hypolimnetic oxygenation on oxygen depletion rates in two water-supply reservoirs. Water Res. 43 (6), 1700–1710. https://doi.org/10.1016/j.watres.2008.12.053.

Gascón Díez, E., Loizeau, J.L., Cosio, C., Bouchet, S., Adatte, T., Amouroux, D., Bravo, A.G., 2016. Role of settling particles on mercury methylation in the oxic water column of freshwater systems. Environ. Sci. Technol. 50 (21), 11672–11679. https://doi.org/10.1021/acs.est.6b03260.

Gilmour, C.C., Podar, M., Bullock, A.L., Graham, A.M., Brown, S.D., Somenahally, A.C., et al., 2013. Mercury methylation by novel microorganisms from new environments. Environ. Sci. Technol. 47 (20), 11810–11820. https://doi.org/10.1021/es403075t.

Herrin, R.T., Lathrop, R.C., Gorski, P.R., Andren, A.W., 1998. Hypolimnetic methylmercury and its uptake by plankton during fall destratification: a key entry point of mercury into lake food chains? Limnol. Oceanogr. 43 (7), 1476–1486. https://doi.org/10.4319/lo.1998.43.7.1476.

Horne, A.J., Jung, R., Lai, H., Faisst, B., Beutel, M., 2019. Hypolimnetic oxygenation 2: oxygen dynamics in a large reservoir with submerged down-flow contact oxygenation (Speece cone). Lake Reservoir Manag. 35 (3), 323–337. https://doi.org/10.1080/10402381.2019.1648612.

Hsu-Kim, H., Eckley, C.S., Achá, D., et al., 2018. Challenges and opportunities for managing aquatic mercury pollution in altered landscapes. Ambio 47, 141–169. https://doi.org/10.1007/s13280-017-1006-7.

Karimi, R., Chen, C.Y., Pickhardt, P.C., Fisher, N.S., Folt, C.L., 2007. Stoichiometric controls of mercury dilution by growth. Proc. Natl. Acad. Sci. U. S. A 104 (18), 7477–7482. https://doi.org/10.1073/pnas.0611261104.

Konopka, A., Brock, T.D., 1978. Effect of temperature on blue-green algae (cyanobacteria) in lake Mendota. Appl. Environ. Microbiol. 36 (4), 572–576.

Krabbenhoft, David, Gilmour, Cynthia, Benoit, Janina, Babiarz, Christopher, Andren, Anders, Hurley, James, 1998. Methyl mercury dynamics in littoral sediments of a temperate seepage lake. Can. J. Fisheries Aquat. Sci. 55, 835–844. https://doi.org/10.1139/cjfas-55-4-835.

Lehman, B., Huff, D., Hayes, S., L, S., 2017. Relationships between Chinook Salmon Swimming performance and water quality in the san Joaquin river, California. Trans. Am. Fish. Soc. 146 (2), 349–358. https://doi.org/10.1080/00028487.2016.1271827.

Lehnherr, Igor, 2014. Methylmercury biogeochemistry: a review with special reference to arctic aquatic ecosystems. Environ. Rev. 22 (3), 229–243. https://doi.org/10.1139/er-2013-0059, 2014.

Matthews, D.A., Babcock, D.B., Nolan, J.G., Prestigiacomo, A.R., Effler, S.W., Driscoll, C.T., Kuhr, K.M., 2013. Whole-lake nitrate addition for control of methylmercury in mercury-contaminated Onondaga Lake, NY. Environ. Res. 125, 52–60. https://doi.org/10.1016/j.envres.2013.03.011.

McCord, S.A., Beutel, M.W., Dent, S.R., Schladow, S.G., 2016. Evaluation of mercury cycling and hypolimnetic oxygenation in mercury-impacted seasonally stratified reservoirs in the Guadalupe River watershed, California. Water Resour. Res. 52 (10), 7726–7743. https://doi.org/10.1002/2016WR019061.

McKee, L., Bonnema, A., David, N., Davis, J.A., Franz, A., Grace, R., Yee, D., 2017. Long-term variation in concentrations and mass loads in a semi-arid watershed influenced by historic mercury mining and urban pollutant sources. Science of The Total Environment 605–606. https://doi.org/10.1016/J.SCITOTENV.2017.04.203, 482–497.

Miklavčič, Ana, Mazej, Darja, Jaćimović, Radojko, Dizdarevic, Tatjana, Horvat, Milena, 2013. Mercury in food items from the Idrija mercury mine area. Environ. Res. 125 https://doi.org/10.1016/j.envres.2013.02.008.

Monson, B.A., 2009. Trend reversal of mercury concentrations in piscivorous fish from Minnesota lakes: 1982-2006. Environ. Sci. Technol. 43 (6), 1750–1755. https://doi.org/10.1021/es8027378, 2009.

Monson, B.A., Staples, D.F., Bhavsar, S.P., et al., 2011. Spatiotemporal trends of mercury in walleye and largemouth bass from the Laurentian Great Lakes region. Ecotoxicology 20 (7), 1555–1567. https://doi.org/10.1007/s10646-011-0715-0, 2011.

Moore, B., Mobley, M., Little, J., Kortmann, B., Gantzer, P., 2015. Aeration and Oxygenation Methods for Stratified Lakes and Reservoirs. NALMS Lakeline.

Nevado, J.J.B., Bermejo, L.F.G., Martin-Dolmeadios, R.C.R., 2003. Distribution of mercury in the aquatic environment at Almaden, Spain. Environ. Pollut. 122, 261–271.

Oremland, R.S., Culbertson, C.W., Winfrey, M.R., 1991. Methylmercury decomposition in sediments and bacterial cultures: involvement of methanogens and sulfate reducers in oxidative demethylation. Appl. Environ. Microbiol. 57 (1), 130–137.

Pickhardt, P.C., Folt, C.L., Chen, C.Y., Klaue, B., Blum, J.D., 2002. Algal blooms reduce the uptake of toxic methylmercury in freshwater food webs. Proc. Natl. Acad. Sci. U. S. A 99 (7), 4419–4423. https://doi.org/10.1073/pnas.072531099.

Pickhardt, P.C., Fisher, N.S., 2007. Accumulation of inorganic and methylmercury by freshwater phytoplankton in two contrasting water bodies. Environ. Sci. Technol. 41 (1), 125–131. https://doi.org/10.1021/es060966w.

Regnell, O., Ewald, G., Lord, E., 1997. Factors controlling temporal variation in methyl mercury levels in sediment and water in a seasonally stratified lake. Limnol. Oceanogr. 42 (8), 1784–1795. https://doi.org/10.4319/lo.1997.42.8.1784.

Rothenberg, S.E., McKee, L., Gilbreath, A., Yee, D., Connor, M., Fu, X., 2010. Wet deposition of mercury within the vicinity of a cement plant before and during cement plant maintenance. Atmos. Environ. 44 (10), 1255–1262. https://doi.org/10.1016/j.atmosenv.2009.12.033.

Seelos, M., 2017. Guadalupe River Watershed Mercury TMDL: 2016-2017 Progress Report on Methylmercury Production and Control Measures. Report by the Santa Clara Valley Water District for the San Francisco Bay Regional Water Quality Control Board.

Singh, S.P., Singh, P., 2015. Effect of temperature and light on the growth of algae species: a review. Renew. Sustain. Energy Rev. 50, 431–444. https://doi.org/10.1016/j.rser.2015.05.024.

Slotton, D.G., Reuter, J.E., Goldman, C.R., 1995. Mercury uptake patterns of biota in a seasonally anoxic northern California reservoir. Water, Air, Soil Pollut. 80, 841–850.

State Water Resources Control Board, 2017a. 2014 and 2016 California Integrated Report Clean Water Act Sections 303(d) and 305(b). Staff Report. October 3.

State Water Resources Control Board, 2017b. Draft Staff Report for Scientific Peer Review for the Amendment to the Water Quality Control Plan for Inland Surface Waters, Enclosed Bays, and Estuaries of California, Mercury Reservoir Provisions — Mercury TMDL and Implementation Program for Reservoirs Statewide Mercury Control Program for Reservoirs (April).

State Water Resources Control Board, 2017c. Draft Staff Report Including Substitute Environmental Documentation: Part 2 of the Water Quality Control Plan for Inland Surface Waters, Enclosed Bays, and Estuaries of California — Tribal and Subsistence Fishing Beneficial Uses and Mercury Provisions.

Stewart, A.R., Saiki, M.K., Kuwabara, J.S., Alpers, C.N., Marvin-DiPasquale, M., Krabbenhoft, D.P., 2008. Influence of plankton mercury dynamics and trophic pathways on mercury concentrations of top predator fish of a mining-impacted reservoir. Can. J. Fish. Aquat. Sci. 65 (11), 2351–2366. https://doi.org/10.1139/F08-140.

Tetra Tech, 2005. Guadalupe River Watershed Mercury TMDL Project Final Conceptual Model Report.
U.S. E.P.A., 1993. Method 300.0, Revision 2.1: Determination of Inorganic Anions by Ion Chromatography.
U.S. E.P.A., 1998. Method 1630. Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS.
U.S. E.P.A., 2002. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry.
U.S. E.P.A., 1996. Method 1669 Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels.
Valdes, C., Black, F.J., Stringham, B., Collins, J.N., Goodman, J.R., Saxton, H.J., et al., 2017. Total mercury and methylmercury response in water, sediment, and biota to destratification of the great Salt lake, Utah, United States. Environ. Sci. Technol. 51 (9), 4887–4896. https://doi.org/10.1021/acs.est.6b05790.
Vlassopoulos, D., Kanematsu, M., Henry, E.A., Goin, J., Leven, A., Glaser, D., et al., 2018. Manganese(iv) oxide amendments reduce methylmercury concentrations in sediment porewater. Environ. Sci.: Processes and Impacts 20 (12), 1746–1760. https://doi.org/10.1039/c7em00583k.
Ward, D.M., Nislow, K.H., Chen, C.Y., Folt, C.L., 2010. Rapid, efficient growth reduces mercury concentrations in stream-Dwelling Atlantic Salmon. Trans. Am. Fish. Soc. 139 (1), 1–10. https://doi.org/10.1577/T09-032.1.
Wu, C., 1986. Jackknife, bootstrap and other resampling methods in regression analysis. Ann. Stat. 14 (4), 1261–1295. Retrieved June 18, 2020, from. www.jstor.org/stable/2241454.
Wu, P., Kainz, M.J., Bravo, A.G., Åkerblom, S., Sonesten, L., Bishop, K., 2019. The importance of bioconcentration into the pelagic food web base for methylmercury biomagnification: a meta-analysis. Sci. Total Environ. 646, 357–367. https://doi.org/10.1016/j.scitotenv.2018.07.328.
Zison, S.W., Mills, W.B., Deimer, D., Chen, Carl, 1978. Rates, Constants, and Kinetics Formulations in Surface Water Quality Modeling. Available from the National Technical Information Service. Springfield VA 22161 as PB-290 938, Report.